

A coupled-cluster study of XNO (X=H,F,Cl): An investigation of weak X-N single bonds

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Timothy J. Lee

NASA Ames Research Center, Moffett Field, California 94035-1000

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Singles and doubles coupled-cluster (CCSD) theory and the CCSD(T) method, CCSD plus a perturbational estimate of the effects of connected triple excitations, have been used to determine the equilibrium structures, dipole moment, vibrational frequencies, and infrared intensities of the HNO, FNO, and ClNO species. A double polarized triple-zeta (TZ2P) quality basis set was used. The CCSD(T) results are found to be in very good agreement with experiment, indicating that the CCSD(T) method performs well in describing the weak X-NO single bond. The experimental heats of formation of the FNO, and ClNO species are examined for internal consistency with experimental data for FNO₂ and ClNO₂, by using an isodesmic reaction. It is concluded that the experimental data exhibit a small inconsistency. An approach, involving in addition the use of homodesmotic reactions, by which a more consistent set of thermochemical data may be obtained is proposed and discussed.

I. INTRODUCTION

It is well known that low levels of *ab initio* theory often do not perform very well for molecules that are composed of several electronegative atoms bonded together. In recent years, however, newly developed techniques have proven to be very reliable in determining the equilibrium structures, dipole moments, vibrational frequencies, infrared (IR) intensities and heats of formation of many molecular species that heretofore were considered to be very difficult to describe properly. For example, the equilibrium structure and fundamental vibrational frequencies of ozone¹ are predicted with high accuracy using atomic natural orbital (ANO) basis sets² in conjunction with the singles and doubles coupled-cluster³⁻⁵ (CCSD) method that includes a perturbational estimate of the effects of connected triple excitations [CCSD(T)].⁶ It is not always appreciated that there are two equally important components that affect the accuracy of any calculation. The series of full configuration interaction studies⁷ performed by the Ames group in the mid 1980s showed that a major limitation in most *ab initio* calculations was the use of small or inadequate one-particle basis sets. Additionally, molecules composed of several electronegative atoms require a high-level treatment of electron correlation. Hence, in order to obtain highly accurate theoretical predictions for these types of molecules it is necessary to use large one-particle basis sets together with a high-level treatment of electron correlation.

A significant component of our current research effort is in the study and elucidation of atmospheric chemistry—particularly those aspects that are involved in ozone depletion. Most of the molecules of interest in this area of research are composed of several electronegative atoms bonded together, and therefore it is important to assess the reliability of the *ab initio* methods that are used in these investigations. We have previously investigated several molecules that possess X-O (where X=H,F,Cl) bonds,⁸⁻¹³ and from comparison with the available experimental data it is apparent that the CCSD(T) method in

conjunction with a one-particle basis set of at least triple-zeta double polarized (TZ2P) quality performs reasonably well in predicting equilibrium structures and vibrational frequencies. It is the purpose of the present paper to investigate the reliability of this level of theory for the study of molecules which possess X-N bonds. The simplest such closed-shell species that are of interest in atmospheric chemistry are the XNO (X=H,F,Cl) molecules, and therefore the present study will focus on these three molecules. The availability of considerable experimental data for these species will aid in our assessment.

The molecular geometry and force field of both FNO and ClNO have been the subject of several theoretical and experimental investigations (for example, see Refs. 14-22). The *ab initio* determination of the equilibrium geometry and quadratic and cubic force constants have been limited to the self-consistent-field (SCF), second-order, and third-order Møller-Plesset perturbation (MP2 and MP3) and configuration interaction (CI) levels of theory with small basis sets.^{14,15} Recently, the equilibrium geometry and harmonic frequencies of FNO have also been evaluated¹⁶ using the singles and doubles quadratic configuration interaction (QCISD) and the QCISD(T) [QCISD plus a perturbational estimate of the effect of triple excitations] methods.²³ In addition, Dibble and Francisco¹⁶ used the CCSD and CCSD(T) methods and small basis sets of polarized triple zeta quality. They obtained reasonable (semiquantitative) agreement with the experimental structure and vibrational frequencies, with the bond distances still in error by ≈ 0.01 Å (N-O) and ≈ 0.02 Å (F-N) and the stretching frequencies in error by ≈ 25 cm⁻¹. Based on experience,⁸⁻¹³ it is likely that the majority of the remaining error is due to deficiencies in the one-particle basis set. It should also be mentioned that Schinke and co-workers^{18,19} have published *ab initio* studies of the photodissociation of ClNO in which a grid of points on the ground state potential energy surface (PES) were evaluated at a high level of theory. However, these grids were centered about the experimental geometry and no *ab initio*

equilibrium structure or force constants were reported.

The experimental structures and force fields of FNO and ClNO are based largely on rovibrational spectra of several isotopomers.^{20,21} For both FNO and ClNO, the "experimental" equilibrium structures and quartic force fields have adopted some low level *ab initio* information in order to perform the rovibrational analysis, and therefore these data should be regarded with caution.

There have been numerous experimental studies of the structure and force field of the HNO molecule as well,²⁴⁻²⁷ although unlike FNO and ClNO, no experimental determination of an equilibrium geometry or quadratic and cubic force field has been reported. Theoretical investigations of the equilibrium geometry and harmonic frequencies of HNO have largely been limited to low level (by today's standards) *ab initio* methods. For example, the equilibrium geometry has been determined at the singles and doubles CI (CISD), MP2, and MP3 levels of theory,²⁸⁻³⁰ with small basis sets. In all of these studies²⁸⁻³⁰ the structure and quadratic force field of the HNO molecule was not of primary interest. In one *ab initio* study³¹ the ground state HNO PES was determined at the externally contracted CI level of theory with a good basis set. The equilibrium geometry obtained was in good agreement with the vibrationally averaged experimental quantity; force field constants were not reported.

As well as the interest in atmospheric chemistry involving the title compounds (for example, see Ref. 32), the HNO molecule is thought to be important in combustion chemistry,²⁹ and in chemical reactions taking place in the exit plume of the space shuttle's primary reaction control system engines.³³ Although the main purpose of the present study has been to document the reliability of theoretical predictions of X-N (X=H, F, and Cl) molecular structures, force fields and energetics that are obtainable using the CCSD(T) electron correlation method in conjunction with large one-particle basis sets, it is also expected that the *ab initio* data will be useful for filling in holes in the experimental information and in the interpretation of future experimental work. Indeed, it is shown below that the interpretation of some past experiments may be improved by using the present theoretical predictions.

II. COMPUTATIONAL METHODS

The equilibrium geometries were determined with a TZ2P basis set at the CCSD and CCSD(T) levels of theory. The TZ2P basis set consists of Dunning's³⁴ [5s3p/3s] contraction of Huzinaga's³⁵ (10s6p/5s) primitive Gaussian functions for (F,O,N) and H, respectively, augmented with two sets of polarization functions³⁶ ($\alpha_d=3.107, 0.855$ for F; $\alpha_d=2.314, 0.645$ for O; $\alpha_d=1.654, 0.469$ for N; $\alpha_p=1.407, 0.388$ for H). The Cl TZ2P basis set is composed of McLean and Chandler's³⁷ [6s5p] contracted functions supplemented with two sets of polarization functions ($\alpha_d=1.072, 0.357$). A previous study¹¹ has shown that little is gained by further uncontraction of the *sp* basis set. For the TZ2P basis set, all six Cartesian components of the *d* functions were included in the basis set. Coupled-cluster

analytical gradient methods^{38,39} were used to locate the equilibrium structure. Quadratic force constants, harmonic frequencies and IR intensities were determined by finite differences of analytical gradients. The dipole moment was determined as the derivative of the energy with respect to an external electric field.

Based on experience⁸⁻¹³ it is expected that the CCSD(T)/TZ2P level of theory will perform very well for the XNO (X=H, F, or Cl) species, yielding bond distances accurate to 0.01–0.02 Å; bond angles accurate to better than 1°; and stretch harmonic frequencies accurate to $\approx 25 \text{ cm}^{-1}$. Even 5 years ago, this type of accuracy would have been considered excellent. However, it is also clear from experience (e.g., see Ref. 1) that the CCSD(T) method is capable of yielding much greater accuracy provided that much larger one-particle basis sets are used. As the very large basis set calculations are significantly more expensive, it is not always necessary to use them if the desired accuracy can be achieved with basis sets of TZ2P quality. The purpose of the present investigation is to explicitly demonstrate how well the CCSD(T)/TZ2P level of theory performs for the XNO (X=H, F, or Cl) species.

In order to assess the reliability of the available experimental thermochemical data, isodesmic reaction energies have been evaluated at the MP2, CCSD, and CCSD(T) levels of theory using ANO basis sets.² The primitive basis sets are van Duijneveldt's⁴⁰ (13s8p/8s) sets augmented with an even tempered sequence of (6d4f/6p4d) polarization functions for (F,O,N) and H, respectively. The polarization function orbital exponents are obtained from $\alpha=2.5^n\alpha_0$; $n=0,\dots,k$ with $\alpha_0=0.16$ and 0.49 for the F *d* and *f* functions, respectively; $\alpha_0=0.13$ and 0.39 for the O *d* and *f* functions; $\alpha_0=0.10$ and 0.30 for the N *d* and *f* functions; $\alpha_0=0.10$ and 0.26 for the H *p* and *d* functions. The Cl primitive basis set is Partridge's⁴¹ (19s14p) set augmented with a (6d4f) set of polarization functions with $\alpha_0=0.06$ and 0.19 for the Cl *d* and *f* functions. The basis set denoted ANO1 consists of 5s4p2d, 4s3p2d, and 4s2p ANOs on Cl, (F,O,N), and H, respectively. The ANO2 basis set is composed of 5s4p2d1f, 4s3p2d1f, and 4s2p1d ANOs on Cl, (F,O,N), and H. For the ANO basis sets, only the spherical harmonic components of the *d*- and *f*-type functions were included.

The coupled-cluster geometry optimizations were performed with the TITAN⁴² program system. The MP2 and coupled-cluster single-point energies were performed with the TITAN coupled-cluster programs interfaced to the SEWARD⁴³ integral program, and the SWEDEN⁴⁴ self-consistent-field and transformation programs. All calculations were performed on either the Computational Chemistry Branch's Convex C210 computer, the NASA Ames Central Computer Facility's Cray Y-MP or the Cray C90.

III. RESULTS AND DISCUSSION

A. Equilibrium structures and vibrational frequencies

The CCSD and CCSD(T) equilibrium structures, dipole moments, harmonic vibrational frequencies and IR intensities of HNO, FNO, and ClNO are reported in Ta-

TABLE I. Total energy (E_h), equilibrium structure, rotational constants (cm^{-1}), dipole moment (D), harmonic frequencies (cm^{-1}), and IR intensities (km/mol) of HNO; obtained with the TZ2P basis set.^a

	CCSD	CCSD(T)	Expt. ^b
E	0.244 761	0.262 793	
μ	1.74	1.72	
\mathcal{T}_1^c	0.016	0.017	
r_{HN}	1.050	1.054	1.063
r_{NO}	1.207	1.219	1.212
$\angle\text{HNO}$	108.0	107.8	108.6
A_e	18.913	18.704	18.476
B_e	1.419	1.394	1.411
C_e	1.320	1.297	1.306
ω_1 H–N str.	2993(113)	2936(126)	2684
ω_2 HNO bend	1631(59)	1583(43)	1565
ω_3 N–O str.	1581(5)	1511(17)	1501

^aThe energy is reported as $-(E+130)$. Bond lengths in Å and angles in degrees. IR absorption intensities in parentheses.

^bVibrationally averaged structure from Refs. 24 and 25; vibrationally averaged rotational constants from Ref. 26; gas-phase fundamental frequencies from Ref. 27. The experimental classification of the HNO bend and the N–O stretch have been reversed—see text for details.

^cSee Ref. 47 for a description of the \mathcal{T}_1 diagnostic.

bles I–III, respectively. Examination of the results for HNO first shows that connected triple excitations increase both bond distances—the H–N distance by 0.004 Å and the N–O distance by 0.012 Å. The HNO angle is only slightly decreased by inclusion of triple excitations. However, triple excitations are found to decrease all of the harmonic frequencies significantly, even the HNO bending frequency. In other words, although the minimum in the bending part of the potential energy surface is only slightly affected, the bending potential is significantly softened by connected triple excitations.

Note that ω_2 has been labeled the HNO bending mode, and ω_3 is labeled the N–O stretch. This classification is based on a potential energy distribution analysis, and al-

TABLE II. Total energy (E_h), equilibrium structure, rotational constants (MHz), dipole moment (D), harmonic frequencies (cm^{-1}), and IR intensities (km/mol) of FNO; obtained with the TZ2P basis set.^a

	CCSD	CCSD(T)	Expt. ^b
E	0.345 395	0.375 843	
μ	1.65	1.85	1.81
\mathcal{T}_1^c	0.022	0.022	
r_{FN}	1.498	1.536	1.517
r_{NO}	1.132	1.137	1.132
$\angle\text{FNO}$	109.9	110.0	109.9
A_e	95 685	93 818	94 962
B_e	12 092	11 643	11 897
C_e	10 735	10 357	10 573
ω_1 N–O str.	1887(239)	1846(244)	1877
ω_2 FNO bend	808(206)	772(178)	775
ω_3 F–N str.	560(148)	520(118)	523

^aThe energy is reported as $-(E+229)$. Bond lengths in Å and angles in degrees. IR absorption intensities in parentheses.

^bEquilibrium geometry, equilibrium rotational constants, and harmonic frequencies from Ref. 21; vibrationally averaged dipole moment from Ref. 22.

^cSee Ref. 47 for a description of the \mathcal{T}_1 diagnostic.

TABLE III. Total energy (E_h), equilibrium structure, rotational constants (MHz), dipole moment (D), harmonic frequencies (cm^{-1}), and IR intensities (km/mol) of ClNO; obtained with the TZ2P basis set.^a

	CCSD	CCSD(T)	Expt. ^b
E	0.339 225	0.370 185	
μ	1.99	2.07	
\mathcal{T}_1^c	0.022	0.022	
r_{ClN}	1.967	2.001	1.975
r_{NO}	1.133	1.141	1.134
$\angle\text{ClNO}$	113.1	113.4	113.3
A_e	86 936	86 066	
B_e	5 795	5 611	5749
C_e	5 432	5 267	5393
ω_1 N–O str.	1850(697)	1804(597)	1836
ω_2 ClNO bend	626(129)	602(95)	603
ω_3 Cl–N str	352(101)	338(64)	336

^aThe energy is reported as $-(E+589)$. Bond lengths in Å and angles in degrees. IR absorption intensities in parentheses.

^bEquilibrium structure, equilibrium rotational constants, and harmonic frequencies from Ref. 20.

^cSee Ref. 47 for a description of the \mathcal{T}_1 diagnostic.

though there is some mixing between the HNO bend and N–O stretch, this mixing is not substantial. This point is discussed because the past experimental classification²⁷ of these modes (ω_2 and ω_3) is reversed from that given in Table I. However, the CCSD(T) ω_2 and ω_3 values are in very good agreement with the experimental fundamental vibrational frequencies, assuming that the anharmonic corrections for these two modes are typical (i.e., 5–10 cm^{-1} for the bending mode and 20–30 cm^{-1} for the N–O stretch). Based on experience,^{8–13} it is likely that the CCSD(T)/TZ2P N–O stretch harmonic frequency is slightly low (≈ 15 –25 cm^{-1}), and comparison with the experimental fundamental supports this assertion. Nonetheless, we believe that the CCSD(T)/TZ2P harmonic frequencies for HNO are accurate enough to conclude that the past experimental classification of these modes is incorrect. However, another and perhaps more convincing test is to compute the harmonic frequencies for DNO as the fundamental vibrational frequencies for this species are also well known. The experimental fundamentals²⁷ for DNO are 2025, 1156, and 1547 cm^{-1} . Using the CCSD(T)/TZ2P quadratic force field yields harmonic frequencies of 2148, 1182, and 1524 cm^{-1} , which are again in very good agreement with the experimental values. Hence, we conclude that the experimental classification of the vibrational modes of HNO was in error.

It is more difficult to assess the reliability of the CCSD(T)/TZ2P harmonic frequency for ω_1 since this mode will have a large anharmonic correction. For example,⁴⁵ the average anharmonic correction for the N–H stretching modes in NH_3 is 164 cm^{-1} . It would thus appear that if the CCSD(T)/TZ2P harmonic frequency is accurate to within ≈ 30 cm^{-1} , as expected based on experience, then the anharmonic correction for this N–H stretch must be substantially larger than found for NH_3 . Comparison of the ammonia N–H stretching fundamentals with the experimental N–H stretching fundamental in HNO shows that the N–H bond in HNO is not typical, and

therefore it may be that the potential energy surface is particularly anharmonic in this region. Resolution of this aspect requires the computation of a full quartic force field, which is beyond the scope of the present study.

Comparison of the CCSD(T) equilibrium structure of HNO with the vibrationally averaged structure shows the expected features based on the discussion of the harmonic frequencies given above. That is the CCSD(T) N–O bond distance is somewhat long (0.007 Å), of which part of this is attributed to vibrational averaging (probably about 0.003 Å) and part to one-particle basis set deficiencies, as discussed in Sec. II. On the other hand, the H–N bond is shorter than the experimental value, which is similar to the situation observed⁴⁶ for HNC. The CCSD(T) HNO angle is in good agreement with the vibrationally averaged value. Hence, it is apparent that the CCSD(T) method performs well for the HNO molecule, and that the weak H–N bond is described reasonably well. The \mathcal{T}_1 diagnostic values⁴⁷ for HNO reported in Table I support the conclusion that the CCSD(T) method should perform well for the HNO molecule.

The FNO and ClNO molecules are a more stringent test, since the X–N bonds in these molecules are even weaker and therefore the bonding is more similar to a loosely coupled pair of radicals. This is precisely the type of bonding that is common among molecules composed of several electronegative atoms, and that is not described very well by low levels of *ab initio* theory. The \mathcal{T}_1 diagnostic values for FNO and ClNO given in Tables II and III indicate that indeed nondynamical electron correlation is more important for these molecules relative to HNO, but they also suggest that the CCSD(T) approach should perform well since molecules with much larger \mathcal{T}_1 values (e.g., O₃, see Ref. 1) are described very well by the CCSD(T) method.

Contrasting the CCSD and CCSD(T) results for FNO shows that connected triple excitations are more important than found for HNO, at least as measured by the effect on the F–N bond distance. This bond is lengthened by 0.038 Å, but the N–O bond distance is only lengthened by 0.005 Å and the FNO angle is only slightly increased. The effect of triple excitations on the harmonic frequencies is, on average, smaller than found for HNO, but for the F–N stretch frequency this is due to the larger mass of the F atom relative to the H atom. In other words, on a percentage basis, the effect of triple excitations on ω_3 of FNO is larger than for any of the harmonic frequencies of HNO. Connected triple excitations have a substantial effect on the dipole moment of FNO, increasing it by 0.2 D.

Comparison of the CCSD(T) results for FNO with the available experimental data shows that the CCSD(T) equilibrium bond distances are slightly too long, which is as expected.^{8–13} As for HNO, the CCSD(T) harmonic frequency for the N–O stretch in FNO is about 20–30 cm^{−1} too low. (We note that there is some uncertainty in the experimental harmonic frequencies²¹ for FNO since some low level *ab initio* data was used in the vibrational analysis.) The CCSD(T)/TZ2P ω_2 and ω_3 values are in excellent agreement with the experimental values. Finally, the

CCSD(T) equilibrium dipole moment value is also in very good agreement with the experimental vibrationally averaged quantity.

Examination of the *ab initio* results for ClNO in Table III shows that the effect of connected triple excitations on the properties of ClNO is intermediate to that observed for FNO and HNO. The Cl–N bond distance is increased by 0.034 Å, while the N–O distance is increased by only 0.008 Å and the ClNO angle is only slightly increased. This is similar to the situation for FNO. However, the effect of triple excitations on the Cl–N harmonic frequency of ClNO is smaller than that found for the F–N harmonic frequency of FNO or, even on a percentage basis, than that found for the H–N harmonic frequency of HNO. The effect of triple excitations on the other two harmonic frequencies of ClNO is similar to that observed for FNO, but the effect on the dipole moment is much smaller for ClNO than for FNO.

As indicated earlier, an experimental equilibrium structure and harmonic frequencies for ClNO are available for comparison, but as for FNO, some low level *ab initio* data were used in the vibrational analysis. The agreement between the CCSD(T) results and the experimental quantities is in general very good. The CCSD(T) N–O stretch harmonic frequency is again slightly low, and the CCSD(T) Cl–N bond distance is slightly long. The agreement for all of the other molecular properties is excellent.

As the CCSD(T)/TZ2P quadratic force fields should be quite accurate, these are presented in Table IV for HNO, FNO, and ClNO. The force fields are presented in simple internal coordinates defined as follows:

$$S_1 = r_{\text{NO}}, \quad (3.1)$$

$$S_2 = r_{\text{XN}}, \quad (3.2)$$

$$S_3 = \angle \text{XNO}, \quad (3.3)$$

where the X in Eqs. (3.2) and (3.3) is H, F, or Cl. Comparison of the CCSD(T) force constants with the experimental values for FNO and ClNO shows that the f_{11} constant is somewhat too small, as expected based on the earlier comparison of harmonic frequencies, but that all of the other unconstrained constants are in good agreement. The CCSD(T) ClNO f_{13} force constant is significantly larger than the “experimental” value, which in fact comes from an SCF calculation. The experimental ClNO force field could no doubt be improved by using the CCSD(T) f_{13} force constant in the vibrational analysis.

To summarize this section, it is evident that the CCSD(T)/TZ2P level of theory performs very well in predicting the molecular structures, quadratic force fields, and dipole moments of the HNO, FNO, and ClNO species. Nothing has been mentioned to this point regarding IR intensities, which is due to a lack of experimental estimates of these quantities. However, in the experimental papers the relative intensities of the various vibrational bands are discussed and the computed IR intensities are in agreement with these qualitative observations.

TABLE IV. Quadratic force constants of HNO, FNO, and ClNO obtained at the CCSD(T)/TZ2P level of theory.^a

	HNO	FNO		ClNO	
	Theory	Theory	Expt. ^b	Theory	Expt. ^c
f_{11}	10.809	15.430	15.912	14.758	15.424
f_{12}	0.877	1.805	1.902	1.238	1.44
f_{22}	4.778	2.131	2.133	1.269	1.254
f_{13}	0.792	0.364	0.323	0.249	0.417
f_{23}	-0.035	0.232	0.236	0.128	0.1505
f_{33}	1.395	1.817	1.841	1.282	1.299

^aUnits are $\text{aJ}/\text{\AA}^2$, $\text{aJ}/\text{\AA} \cdot \text{rad}$, and aJ/rad^2 . See text for definition of the internal coordinates.^bReference 21; some cubic force constants were constrained to *ab initio* values in the refinement.^cReference 20; f_{13} constrained to have a value obtained from SCF *ab initio* calculations.

B. Heats of formation and homodesmotic reactions

Experimental estimates of the heat of formation⁴⁸ are available for HNO, FNO, and ClNO. The reliability of these data may be examined by computing the reaction energy of a suitable set of isodesmotic reactions and then checking the internal consistency of the experimental thermochemical data. *Ab initio* methods are particularly well suited to this approach for testing the reliability of the experimental data since isodesmotic reaction energies are usually determined accurately even with low level methods. The isodesmotic reactions to be considered are given below:



Unfortunately, there is no experimental determination of the heat of formation of HNO_2 , and so reactions (3.4) and (3.5) cannot be used to assess the experimental heats of formation of XNO ($X = \text{H}, \text{F}, \text{or Cl}$). However, there are experimental data available for the reactants and products of reaction (3.6), and so it is possible to use this isodesmotic reaction. The equilibrium structures and harmonic frequencies of the FNO_2 and ClNO_2 species have been determined at the CCSD(T)/TZ2P level of theory—the structure for FNO_2 is not that much different from the results presented in Ref. 10 (where a slightly different TZ2P basis set was used) while the CCSD(T) results for ClNO_2 are published separately⁴⁹ (in a study that also includes the *cis*- and *trans*-ClONO isomers). Reaction energies for ΔE_3 were computed using the CCSD(T)/TZ2P equilibrium geometries and the ANO1 and ANO2 basis sets described previously. The computed reaction energies are summarized in Table V. While ΔE_3 is fairly insensitive to improvements in the basis set and the treatment of electron correlation, it is important to point out that a variation of at least 1.5 kcal/mol does occur. Hence, even when using isodesmotic reactions, for compounds composed of several electronegative atoms bonded together it is best to use the highest level of theory available. In this case, the last row of Table V contains the most reliable value. Using CCSD(T)/TZ2P harmonic frequencies, a zero-point vi-

brational energy contribution of 0.3 kcal/mol is computed for reaction (3.6). Adding this to the value in the last row of Table V yields 2.7 kcal/mol as our best estimate for ΔE_3 at 0 K. Using the available experimental heats of formation⁴⁸ (at 0 K) leads to a value of -0.8 kcal/mol for the reaction energy. The agreement between theory and experiment is reasonable, although the difference—3.5 kcal/mol—is larger than would be expected for the levels of theory used here, suggesting that small errors exist in some of the experimental thermochemical data. This is not an unusual situation for molecules composed of several electronegative atoms bonded together—indeed the generally accepted heat of formation of *cis*-FONO was recently shown¹⁰ to be in error by ≈ 25 kcal/mol, and Pople and Curtiss⁵⁰ have recently suggested a revised heat of formation for HOF that differs from the old value by ≈ 3 kcal/mol.

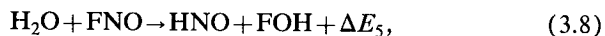
Although it is clear that some of the experimental heats of formation for the molecules involved in reaction (3.6) are inaccurate, it is not easily shown which values are in error, and by how much. Given the stated uncertainties in the experimental data, it is likely that the heat of formation of the FNO_2 species has the largest error, but this is not certain. Nevertheless, it is clear that relying on only isodesmotic reactions to determine the heats of formation of new species is not sufficient due to the lack of accurate experimental heats of formation. It is important to know very accurate heats of formation (i.e., $< \pm 1.0$ kcal/

TABLE V. Energies (kcal/mol) for reactions (3.6), (3.7), (3.8), and (3.9). CCSD(T)/TZ2P geometries were used.^a

	ΔE_3	ΔE_4	ΔE_5	ΔE_6
MP2/ANO1	1.5	59.3	89.8	30.5
MP2/ANO2	1.7	56.7	88.8	32.1
CCSD/ANO1	2.5	50.7	80.3	29.6
CCSD/ANO2	2.7	48.2	79.4	31.2
CCSD(T)/TZ2P	3.0	54.2	82.3	28.1
CCSD(T)/ANO1	2.3	54.2	82.1	27.9
CCSD(T)/ANO2	2.4	51.8	81.1	29.3

^aZero-point vibrational energies not included—see text for energy differences where these are included.

mol uncertainty) for molecules of interest in atmospheric chemistry in order to determine accurate thermal dissociation rates. For example, it is desirable to know the ClO–OCl bond energy to $\approx \pm 0.2$ kcal/mol (see Ref. 11 for a discussion of this bond energy). Thus, it is proposed to use, in addition, reactions in which species such as H, F, and Cl are interchanged. Consider the following reactions:



In these reactions, the X–N and Y–O bonds in the reactants are balanced by the Y–N and X–O bonds in the products (X, Y = H, F, Cl); this type of reaction is referred to as an homodesmotic reaction. Clearly, homodesmotic reactions will not exhibit the same degree of cancellation of errors that typify isodesmotic reactions. However, it is hoped that the nitrogen and oxygen bonding of these elements is similar enough that a large degree of cancellation will occur. If so, then it will be possible to assess more precisely the reliability of experimental heats of formation. The first step is to compute reaction energies for (3.7)–(3.9) using different levels of theory so that the sensitivity with respect to basis set and electron correlation may be determined. These results are also presented in Table V [CCSD(T)/TZ2P geometries were used]. As can be seen, the range of values is much larger than found for typical isodesmotic reactions, however, considering only the CCSD and CCSD(T) results this variation is greatly reduced. Furthermore, comparison of the CCSD/ANO2 and CCSD(T)/ANO2 values shows that the triples correction is in general not too large—especially for reactions (3.8) and (3.9). One additional feature of the results in Table V should be noted—that the variation of ΔE_6 with respect to level of theory is much smaller than for either ΔE_4 or ΔE_5 , which is no doubt because F and Cl bonding is much more similar to one another than to H bonding.

A further test of this new approach is to compare our best computed reaction energies (3.7)–(3.9) to those determined from experimental heats of formation. Using CCSD(T)/TZ2P harmonic frequencies, zero-point corrections of -0.6 , -0.7 , and -0.2 kcal/mol are obtained for reactions (3.7)–(3.9), respectively. Note that small zero-point corrections are a feature of isodesmotic reactions—the small values here for reactions (3.7)–(3.9) are indicative of a balanced cancellation of errors. Adding the zero-point corrections to the values in the last row of Table V yields 51.2, 80.4, and 29.1 kcal/mol as the best computed estimates (at 0 K) for ΔE_4 , ΔE_5 , and ΔE_6 . Using experimental heats of formation (at 0 K; HOF from Ref. 50, all others from Ref. 48) gives values of 51.7, 76.9, and 25.2 kcal/mol. The difference between theory and experiment for reactions (3.7)–(3.9) is considerably smaller than found for reactions (3.4)–(3.6), lending further support to the new method proposed here, and to the assertion that the XNO₂ experimental thermochemical data have larger errors than the XNO experimental thermochemical data.

Thus it appears that this approach may be useful to aid in determining an internally consistent set of thermochemical data for molecules of atmospheric interest.

IV. CONCLUSIONS

The equilibrium structures, dipole moments, harmonic vibrational frequencies, and IR intensities of HNO, FNO, and ClNO have been determined at the CCSD and CCSD(T) levels of theory using a TZ2P basis set. The CCSD(T) equilibrium structures and harmonic frequencies are in good agreement with the available experimental values. It is therefore concluded that the CCSD(T) level of theory, in conjunction with a large one-particle basis set, provides an accurate description of weak X–N (X = H, F, Cl) single bonds.

The experimental classification of vibrational modes in HNO is found to be in error—that is ν_2 should be labeled the HNO bend while ν_3 is the N–O stretch. The excellent agreement between the computed harmonic frequencies of DNO and the experimental fundamentals provides support for the new vibrational mode descriptions.

Using an isodesmotic reaction involving the XNO and XNO₂ (X = F, Cl) species, it is shown that there are some inaccuracies in the available experimental heats of formation for this set of molecules. It is likely that the major error exist for the FNO₂ species, and the good agreement between theory and experiment for the ΔE_4 , ΔE_5 , and ΔE_6 quantities supports this assertion. However, it is likely that some small inaccuracies are also present in the experimental heats of formation of the XNO species. A new method for examining the heats of formation of molecules of atmospheric interest is proposed and examined. This new approach is based on the similarity of X–N and X–O bonding and involves the use of homodesmotic reactions. It is shown that while homodesmotic reaction energies do not exhibit the same degree of cancellation of errors that typify isodesmotic reactions, the cancellation of errors is still good—especially when high levels of theory are used.

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